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Effect of Sampling Technique on the Measurement of Gasoline Volatility

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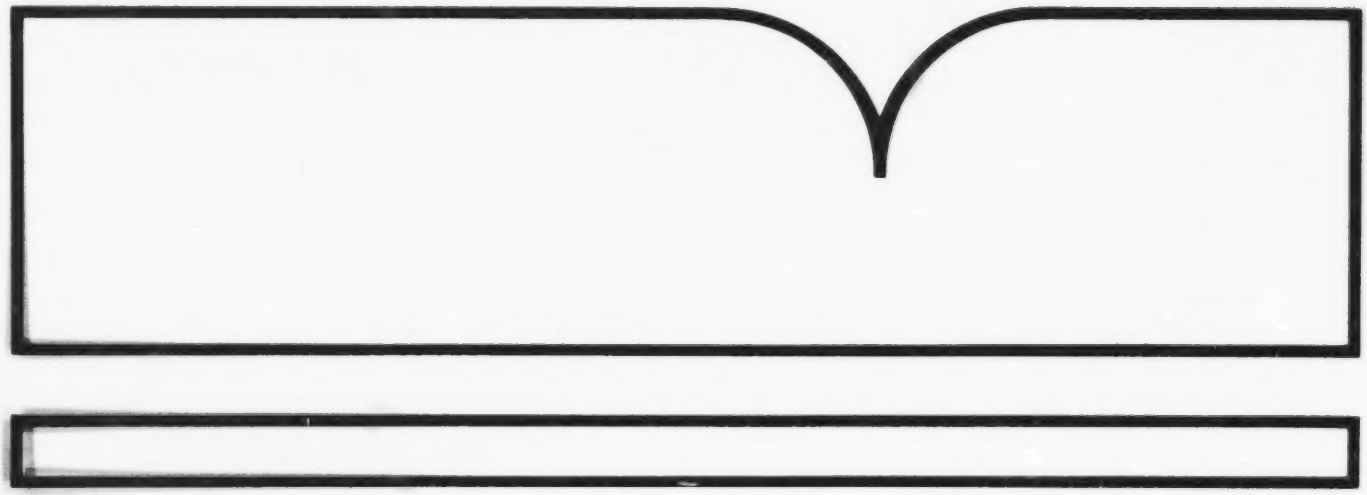

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Technical Report

The Effect of Sampling Technique on the Measurement of Gasoline Volatility

July 1987

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John T. White

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16. ABSTRACT

The U.S. Environmental Protection Agency is proposing the adoption of regulations which would reduce the amount of hydrocarbons released to the atmosphere due to evaporation of gasoline. One regulatory alternative under consideration is to put an upper limit on volatility. Volatility is typically quantified by measurement of Reid vapor pressure. Although established procedures exist for the sampling of fuel and measurement of this parameter, there is concern about their utility and efficiency in large-scale monitoring and enforcement situations.

The purpose of this report was to identify and quantify any differences in vapor pressure caused by the technique used to obtain the sample. The objective of this effort is identify and document a fast, inexpensive, and reliable method to obtain enforcement-quality samples at service station-type facilities. This report examines the effect of four sampling techniques and two methods of analysis on three types of fuels. Also evaluated as a part of this study were the effect of storage temperature on samples, losses due to residence time in the dispensing system and the time required to perform each of the sampling techniques.

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Abstract

The U.S. Environmental Protection Agency is proposing the adoption of regulations which would reduce the amount of hydrocarbons released to the atmosphere due to evaporation of gasoline. One regulatory alternative under consideration is to put an upper limit on volatility. Volatility is typically quantified by measurement of Reid vapor pressure. Although established procedures exist for the sampling of fuel and measurement of this parameter, there is concern about their utility and efficiency in large-scale monitoring and enforcement situations.

The purpose of this program was to identify and quantify any differences in vapor pressure caused by the technique used to obtain the sample. The objective of this effort is to identify and document a fast, inexpensive, and reliable method to obtain enforcement-quality samples at service station-type facilities.

This program evaluated the effect of four sampling techniques and two methods of analysis on three types of fuels. Six samples for each condition resulted in a total of 144 data points. One of the four sampling methods is described in ASTM D 4057, "Standard Practice for Manual Sampling of Petroleum and Petroleum Products." This technique is found in paragraph 9.2.3.1 as the all-levels method (one-way) for tank sampling. The other three sampling methods employed the standard dispensing nozzle with varying means, e.g., bottom-filling and chilling, to prevent the loss of lighter components. One of the two methods of analysis was found in ASTM P 176, a proposed specification for gasolines which is intended to replace ASTM D 439 standard. ASTM P 176 contains an updated version of ASTM D 323 (the traditional method of measuring vapor pressure). The other method was a semi-automated version which uses an instrument manufactured by Herzog. Two of the three fuels used were standard gasolines used in vehicle testing at EPA's Motor Vehicle Emissions Laboratory. The other was a sample of gasohol obtained from a local service station.

Also evaluated as a part of this study were the effect of storage temperature on samples, losses due to residence time in the dispensing system and the time required to perform each of the sampling techniques.

The work was conducted during the fall of 1986. The results indicate that there is no practical difference between the volatility of a sample taken from a dispensing nozzle and the volatility of one taken from the underground tank. This finding applied over the range of fuels and the two methods of analyses. Purge volume had no effect on the nozzle sample for the ambient conditions at the time of the study.

Background

As control of exhaust and evaporative emissions from motor vehicles has progressed, the percentage of air pollution resulting from emissions from the evaporation of gasoline has increased. Exacerbating this trend is the fact that volatility of typical gasolines has increased steadily over the past fifteen years, with the most significant increases in the last five. These increases are caused by lighter and less expensive components which are being used to maintain octane ratings as lead is phased out. The result of higher volatility is more emissions from all stages in the distribution chain as well as those from vehicles themselves.

EPA is studying a number of efforts to minimize the release of gasoline vapors. Two of the most notable are vapor recovery, either by the vehicle (known as "on-board") or at the pump (known as "Stage II"), and restrictions on the volatility of commercial gasoline. Although established procedures exist for the sampling of fuel and the measurement of volatility, there is concern about the utility and efficiency of these procedures in a large scale monitoring and enforcement situation. Sampling for volatility must be done to minimize the loss of those components that have the greatest effect on a fuel's vapor pressure. All sampling methods, including ASTM methods, are subject to errors which will tend toward lower vapor pressure measured in the sample versus the true vapor pressure of the product.

Purpose

The purpose of this program was to identify and quantify any differences in volatility caused by the technique used to obtain the sample. The result of this effort is intended to identify and document a fast, inexpensive, and reliable method to obtain samples for monitoring and enforcement actions.

Program Design

Methods of Analysis:

Historically, volatility has been associated with the results of a test for vapor pressure using the Reid method. This test was adopted by the American Society for Testing and Materials (ASTM) in 1930 and is documented in their procedure D 323. A reference to Reid vapor pressure (RVP) implies this test procedure, which prescribes a closed cylinder and the measurement of the pressure above a sample which has been heated from 32°F to 100°F. RVP values are typically expressed in pounds per square inch (psi). Because it involves a traditional procedure which addresses volatility in a typical range of ambient temperatures, RVP is the parameter which was examined during this program. Two test procedures, both based on ASTM D 323, were used.

One procedure, known as the "dry" method, is contained in ASTM's 1986 Annual Book of Standards as part of P 176, "Proposed Specification for Automotive Spark-Ignition Engine Fuel." It is described in Annex A3, "Proposed Test Method for Vapor Pressure of Spark Ignition Engine Fuel (Dry method)." This procedure is analogous to ASTM D 323 in almost all respects, the differences lying in the handling of the vapor chamber and sample chamber

to minimize contact of the sample with the water used in the process. The procedure also prescribes a test to determine if water did contaminate the sample during the analysis. These changes in D 323 were deemed necessary since alcohol/gasoline blends are sensitive to water and could undergo a phase separation in the assembled vapor pressure bomb which might reduce measured volatility.

The other procedure is known as the "Herzog" method. The title refers to the manufacturer of the instrument designed to perform ASTM D 323 in a semi-automated manner.* Handling of samples for analysis on this machine was also modified to prevent water from affecting the readings. It is used by some refiners and laboratories and is expected to be formally accepted by ASTM as an equivalent method in the near future. Use of this instrument gives the analyst a 30-50% improvement in the time required for an analysis.

Fuels:

A total of three types of fuel were chosen for the evaluation of sampling techniques, two gasolines routinely used in EPA testing and one gasohol (nominally 10% ethanol and 90% unleaded gasoline) obtained from a local service station.

The "Unleaded Test Gasoline (96 RON)" used as one of the fuels is the primary test gasoline at the EPA Motor Vehicle Emission Laboratory (MVEL). It is used in Certification and Recall testing of Light Duty vehicles in accordance with the Federal Test Procedure. The specifications for this fuel are stringent but were originally based on typical high octane summer grade gasoline in the late 1960's. The CFR specifies the RVP to be within a range of 8.7 to 9.2 psi.

The second gasoline, "Unleaded Test Gasoline (Commercial)," is designed to represent a typical modern gasoline of intermediate volatility (the procurement specification for RVP is 11.5-12.0 psi). It is used at MVEL as one of the fuels in the Emission Factors Testing Program. This fuel was also used in the portion of the study which evaluated the effect of weathering.

Gasohol was chosen for the third fuel to evaluate the ability of the analysis methods and sampling techniques to properly address a typical oxygenated blend. The samples were obtained from a local service station where the product is sold as "Super Unleaded" and is labeled as containing ethanol.

Neo-Hexane, a pure component with known volatility, was also used as a reference standard. Its RVP is 9.86 psi.

"Fleet Gasoline" was used for the portion of the study which addressed purge volume. This is a commercial fuel used at MVEL for various purposes. It is a seasonal, non-oxygenated, unleaded regular grade gasoline. The current batch had an RVP of 12.2 psi. It was chosen because of its high volatility,

* Walter Herzog GMBH, Fabrik fur Laboratoriumsapparate, D 6970 Lauda; Badstrabe, 3 - 5, West Germany.

making it more sensitive to sampling and weathering phenomena, and the similarity of its dispensing system to normal commercial equipment.

Sampling Techniques:

Four different techniques were used to obtain the samples, one from the underground storage tank and three from the dispensing nozzle. Sampling from various levels throughout the underground tank using a chain and special flasks was based on the All-Levels Sample (one-way) for tank sampling specified in Section 9.2.3 of ASTM D 4057, "Standard Practice for Manual Sampling of Petroleum and Petroleum Products." For the purpose of this evaluation, this technique will be known as "ASTM." This is considered to be the "official" method and is thought to provide the best representation of the fuel in a tank. However, from the monitoring and enforcement standpoint, a technique involving underground tanks is time-consuming and may be extremely difficult to perform, especially on tanks with the submerged drop tubes required by Stage I vapor recovery requirements.

One of the three nozzle techniques was performed in accordance with California Air Resources Board (CARB) regulations under Section 2261 of Title 13. It uses a simple nozzle extender which directs the flow to the bottom of a chilled one-quart metal container. Another technique is one that is same as above but foregoes the chilled container. They are referred to as "CARB" and "Ambient," respectively.

The third nozzle technique was one which has been employed at MVEL and will be known as the EPA technique. It uses an adapter that attaches to the nozzle and directs the flow through 25 feet of 1/4-inch copper tubing. The coil of tubing is packed in crushed ice to chill the sample before it reaches the sample container. The outlet of the tubing is fitted to a stopper in a manner that bottom-fills the container. The container is also packed in crushed ice. At MVEL, the container normally used for this procedure is a one-quart glass bottle. To reduce the number of variables in the study, metal containers with necks that could accept the CARB sampling device were used for each of the nozzle techniques.

In each of the four cases above, the sample was drawn to 70%-80% of the capacity of the one-quart container. Each can was sealed immediately and stored on ice or refrigerated until analysis. There was no transfer of samples between the time of sampling and the time of analysis. Each container was examined upon filling and before reopening to ensure a proper seal.

Number of Samples:

A total of six samples in each condition was chosen to achieve a balance between the amount of time and effort required and the statistical significance desired. Thus, six samples of three fuels using four sampling techniques and two methods of analysis resulted in 144 samples.

Additional Features:

Two other aspects of the issue were also examined as a part of this

project. One was "weathering" of the samples, as would occur in a real-world situation where shipping and storage preceded the analysis. This subject was studied by obtaining 132 identical samples of Unleaded Test Gasoline (commercial) and storing 60 samples at 40°F, and 60 at 80°F. Twelve were analyzed immediately, six using P176 and six by the Herzog "dry method." The stored samples were analyzed after 5, 9, 14, 28, and 59 days. In this process, one-quart cans were filled to 70-80% of capacity using the "Ambient" sampling methodology.

The last aspect of this study is purge volume and its effect on measured vapor pressure. It is possible that the volatility of fuel that has remained within a dispensing system may not properly represent the volatility of the fuel in the underground tank. This study sampled fuel from an outdoor dispenser at MVEL. This dispenser was not used over a period of 12-24 hours before each set of three samples were drawn. The samples consisted of six sets of three samples of which one was a tank sample, drawn as in the earlier study; a nozzle sample with no purge; and a nozzle sample from the same dispenser after a discharge of three gallons.

Conduct of the Program

Preliminary work was conducted during July and August of 1986. The actual sampling and analysis were performed from August 18 through September 7. In general, the program proceeded smoothly. A sufficient number of sampling flasks were fabricated and suitable one quart cans from the same lot were readily available.

The CARB, Ambient and EPA sampling techniques proved to be straightforward. For the ASTM technique, we received good cooperation from Gallup-Silkworth, a local fuel distributor who also operates a number of service stations. One of their stations was the source of the gasohol samples which were found to contain 9% ethanol.

The adaptations of the Herzog and D 323 measurement apparatus to permit analyses by the "dry" method were found to be minor. The only major difficulty encountered in the conduct of the program was a problem with the temperature controller on the manual bath. We could not maintain 100°F and, therefore, were unable to perform P 176. As a result, 63 of the 72 P 176 samples had to be stored for almost two weeks before this problem was corrected.

Results

Attachment A, "Results of Individual Analyses for Vapor Pressure," displays the values from each of the 144 samples which were the primary focus of this project. The results on each of the three fuels are sorted by the four sampling techniques within the two analysis procedures. The mean and standard deviations from the six samples in each of the 24 groups are shown.

Attachment B, "Summary of Results," is a table presenting these results in a manner which allows a comparison of the Herzog procedure to the ASTM P 176 Procedure for each type of fuel.

Attachment C, "Analysis of Neo-Hexane," displays the results of the analyses of twelve samples of Neo-hexane, a pure component of gasoline with a known vapor pressure. Six samples were analyzed by each procedure to establish a measure of accuracy.

Attachment D, "Evaluation of Storage Conditions on Vapor Pressure," contains the results on the lot of 132 samples; groups of them were analyzed at 0, 5, 9, 15, 28, and 59 days.

Attachment E, "Effect of Purge Volume," contains the result of the analyses of the 18 samples.

Attachment F, "Estimated Time for Various Sampling Scenarios," is based on our experience with the four techniques. It will be useful in planning enforcement activities.

Discussion

The statistics discussed in the following sections are based on results from MIDAS, the statistical package available through the Michigan Terminal System. The basic program is a univariate, one-way, analysis of variance (ANOVA) which was performed to identify significant differences in the average performances. The 95% confidence level was chosen.

Sampling Techniques:

The data on individual samples as shown in Attachment A permitted a comparison of the four sampling techniques and two methods of analysis on each of the three fuels.

In general, the P 176 procedure resulted in less precision (higher standard deviations) than the corresponding analyses using the Herzog instrument. There can be several possible reasons for this phenomenon:

1. An inherent advantage to the semi-automated method.

2. Our inexperience with the P 176 technique and the number of samples to be analyzed in such a short period.

3. Problems with the samples themselves, since most of them had to be stored for almost two weeks while the bath was not operating properly.

This latter reason is supported by the fact that the greatest precision for the P 176 Procedure was achieved on the only full set of samples, which was analyzed promptly after sampling. This was the set taken from Tank 7 using the ASTM sampling technique.

The statistical analysis of the P 176 data showed the results from the Ambient technique on the Unleaded Test Gasoline (96 RON) were significantly higher than each of the other three techniques.

For the Herzog method, the following significant differences were found:

1. For Unleaded Test Gasoline (96 RON), the CARB technique had higher results than the Ambient technique.

2. For Unleaded Test Gasoline (Commercial), the EPA technique showed higher results than each of the other three.

3. For the Super Unleaded Gasoline (Gasohol), the ASTM technique had higher results than the EPA or CARB techniques.

Notwithstanding the statistical significance of the findings, it appears that any of the nozzle techniques can be employed to obtain a representative sample of a typical gasoline.

Comparison of the Two Methods of Analysis:

The data in Attachments B, C, and D were analyzed statistically to determine any differences between the Herzog "dry" method and the manual tank and gauges. The data from the sampling technique of this study indicated better precision and a positive bias of the Herzog method vs. the manual method.

The data generated during the sample weathering study and the measurement of neo-hexane displayed no significant difference except in precision. The Herzog, once again, displayed better precision over the manual tank and gauges.

Upon reviewing the above data in light of the precision from other EPA and ASTM Correlation efforts, it was observed that none of the differences were greater than the published repeatability; therefore, the two methods can be considered essentially equivalent.

Sample "Weathering:"

Presuming that most samples obtained for use in enforcement situations will not be analyzed immediately and that continuous storage in a chilled condition is unfeasible, a part of this project was designed to assess any loss in vapor pressure due to "weathering." The fuel chosen for this experiment was the Unleaded Test Gasoline (Commercial). Its relatively high vapor pressure increases the sensitivity of the experimental condition. In this project, care was taken, e.g. leak checks, to ensure that any changes were due solely to the temperature. The results in Attachment D indicate that the refrigerated samples and the non-refrigerated ones did not produce significantly different results over the total storage period.

Evaluation of "Purge Volume:"

Along with weathering, another concern is the possible difference in volatility between the stored fuel and that obtained by a nozzle sample without first purging a quantity of gasoline through the dispenser and its supply lines. We chose to evaluate this situation using a gasoline with a 12.2 psi Reid Vapor pressure at MVEL where the fuel would be dispensed through the

course of a day. A set of three samples was obtained after the dispenser was not used for 12 hours to 24 hours. One was a tank sample using the ASTM method. The other two were nozzle samples using the Ambient method. The first sample was taken from the dispenser nozzle before any gasoline was pumped through the dispenser. Three gallons of the gasoline were discarded prior to the second sample. The third sample was the tank sample. This set of three samples were taken over a six-day period for a total of 18 samples. The samples were then analyzed using the Herzog "dry" method.

The results in Attachment E indicate that, under the ambient conditions at MVEL during the sampling (60°F-75°F), there is no difference between the tank sample and the nozzle samples.

Time Required for Various Sampling Techniques:

The times estimated in Attachment F are based on our experiences during the course of this project. As can be seen, there is a wide range in the amount of overhead required, although the times to obtain successive samples are similar. The results from the vapor pressure analyses indicate that the ASTM method does not have any advantage when evaluating typical gasolines. Moreover, tank sampling requires active cooperation by the service station operator, e.g., removal of drop tube.

Choice of Containers:

A minor difficulty involved the use of the rectangular metal can used in our application of the CARB method. These cans are about 7" tall, 4" wide and 2.25" deep. They have a flat top with a 1.75" screw-on cap with a waxed cardboard insert. Our technique for sealing was finger tight plus one-sixteenth to one-eighth of a turn with a pipe wrench. In general, they appear to be able to store gasoline without leakage. However, using the chilling techniques which involve ice invariably resulted in a pool of water on the top of the can. Some of this water was retained in the joint between the cap and the threads on the can. As the can was opened, the vacuum created by the cooled vapor caused some water to be drawn inside. The phenomenon was thought to be the source of a few drops of water which were found in a number of samples. Use of more rigid containers with sloping necks would probably minimize the problem. The effect of a small amount of water on the results is uncertain but is expected to be insignificant with pure gasoline and cause only a slight decrease in vapor pressure with alcohol blends.

Rigidity of containers may be more important than neck profile. The collapse and subsequent expansion of the can sides, in concert with their large cap thread area, is probably most responsible for water from the ice baths entering the samples. Also, chilled samples placed in a warmer (40°F) refrigerator results in a positive pressure on the container's cap, whereas ambient temperature samples placed in a chilled environment result in negative pressure, causing a better seal.

Conclusions

1. Each of the three sampling techniques which draw fuel from the dispensing nozzle resulted in a representative sample of the contents of the underground tank.

2. Although some additional care was required, proper samples of alcohol-gasoline blends were obtained in a manner similar to gasoline.

3. Purging of the dispensing system was not a factor in the measured volatility of the fuels.

4. Storage time and temperature had no measurable effect on the volatility of the sample.

Attachment A

ENGINEERING OPERATIONS DIVISION

The Effect of Sampling Technique on the Measurement of Gasoline Volatility

Results of Individual Analyses for Reid Vapor Pressure

	ASTM P 176 (the "dry" counterpart of ASTM D 323)				Herzog (Automated dry method based on D 323)			
Name:	**ASTM**	**EPA**	**CARB**	**Ambient**	**ASTM**	**EPA**	**CARB**	**Ambient**
Source:	Tank	Nozzle	Nozzle	Nozzle	Tank	Nozzle	Nozzle	Nozzle
Container:	Flask	Can	Can	Can	Flask	Can	Can	Can
Temperature:	Ambient	Chilled	Chilled	Ambient	Ambient	Chilled	Chilled	Ambient
Technique:	Dipped into underground tank.	Bottom filled thru chilled tubing	Bottom filled using nozzle extension	Bottom filled using nozzle extension	Dipped into underground tank.	Bottom filled thru chilled tubing	Bottom filled using nozzle extension	Bottom filled using nozzle extension
Unleaded	8.59	8.76	8.58	8.65	9.02	8.93	8.92	8.89
Test	8.54	8.72	8.67	8.79	8.93	8.94	8.95	8.90
Gasoline	8.75	8.93	8.54	8.92	8.96	8.93	8.95	8.91
(96 RON)	8.71	8.52	8.67	9.05	8.89	8.90	8.98	8.88
	8.39	8.80	8.36	9.02	8.86	9.01	8.89	8.86
EPA Tank 8	8.45	8.56	8.45	9.01	8.94	8.86	8.98	8.88
Mean:	**8.57**	**8.72**	**8.55**	**8.91**	**8.93**	**8.93**	**8.95**	**8.89**
Std. Dev.:	0.14	0.15	0.12	0.16	0.06	0.05	0.04	0.02
Unleaded	11.82	11.68	11.24	11.85	12.04	12.17	12.00	12.11
Test	11.81	11.92	12.04	12.38	12.17	12.09	11.95	12.04
Gasoline	11.91	11.36	11.67	11.71	12.07	12.12	12.00	12.03
(Comm.)	11.86	11.83	11.66	11.41	11.93	12.15	12.07	11.99
	11.94	11.85	11.74	11.73	11.95	12.09	12.00	12.09
EPA Tank 7	11.72	11.88	11.73	11.71	11.99	12.16	11.92	12.03
Mean:	**11.84**	**11.75**	**11.68**	**11.80**	**12.03**	**12.13**	**11.99**	**12.05**
Std. Dev.:	0.08	0.21	0.26	0.32	0.09	0.04	0.05	0.04
Super	12.63	12.78	12.93	12.89	13.07	12.80	12.82	12.88
Unleaded	12.66	11.87	12.87	12.71	12.93	12.80	12.84	12.79
Gasoline	12.82	12.67	12.54	12.05	12.86	12.81	12.47	12.79
(Gasohol)	12.77	12.33	12.68	12.21	12.94	12.83	12.73	12.81
	12.91	12.29	12.64	12.37	12.91	12.89	12.88	12.80
Local Dealer	12.89	12.80	12.62	12.64	13.04	12.88	12.95	12.95
Mean:	**12.78**	**12.46**	**12.71**	**12.48**	**12.96**	**12.84**	**12.78**	**12.84**
Std. Dev.:	0.12	0.36	0.15	0.32	0.08	0.04	0.17	0.07

Note: Values shown above are expressed in psi.

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Attachment C

ENGINEERING OPERATIONS DIVISION

The Effect of Sampling Technique on the Measurement of Gasoline Volatility

Analysis of Neo-Hexane (A pure compound of known volatility)

Method	Results on Individual Samples						Mean	Std Dev	Diff.
ASTM P 176	9.80	9.80	9.78	9.63	9.91	9.80	**9.79**	0.09	**-0.07**
Herzog	9.96	9.91	9.91	9.89	9.81	9.79	**9.88**	0.07	**0.02**

Note: Neo-Hexane has an RVP of 9.86. The results above are expressed in psi.

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Attachment D

ENGINEERING OPERATIONS DIVISION

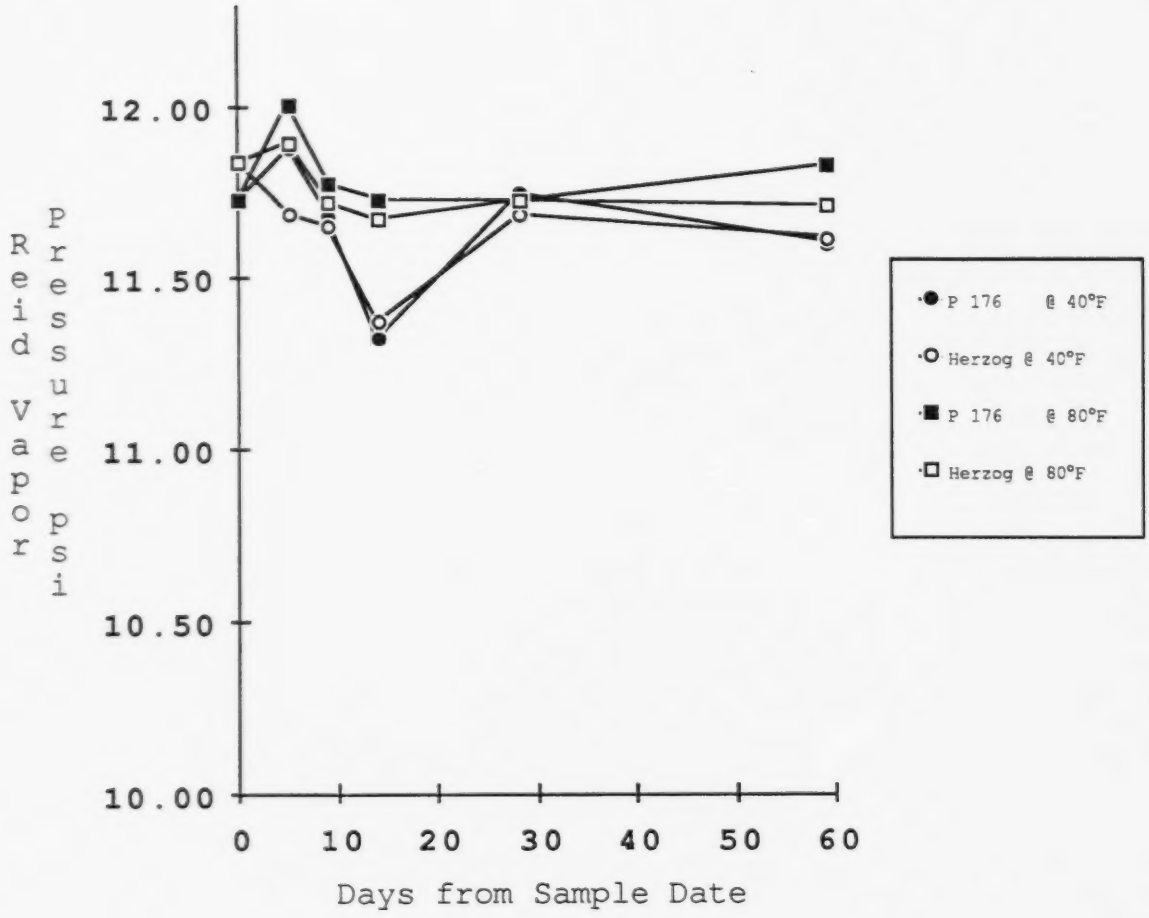
The Effect of Sampling Technique on the Measurement of Gasoline Volatility
Evaluation of Storage Conditions on Vapor Pressure

Storage Temperature:	Analyzed Imediately		40°F	40°F	80°F	80°F
Method of Analysis:	Herzog	P 176	Herzog	P 176	Herzog	P 176
Analysis Date:	19-Feb	19-Feb	24-Feb	24-Feb	24-Feb	24-Feb
Days Since Sampled:	0	0	5	5	5	5
	11.67	11.74	11.70	12.29	11.78	12.46
	11.79	12.02	11.57	11.52	12.13	11.93
	11.71	11.66	11.75	11.60	11.85	11.91
	11.70	12.01	11.82	11.76	11.90	12.22
	11.78	11.89	11.62	12.22	11.84	12.05
	11.73	11.73			11.92	11.46
Mean:	**11.73**	**11.84**	**11.69**	**11.88**	**11.90**	**12.01**
Standard Deviation:	0.047	0.154	0.100	0.356	0.121	0.337

Storage Temperature:	40°F	40°F	80°F	80°F	40°F	40°F	80°F	80°F
Method of Analysis:	Herzog	P 176	Herzog	P 176	Herzog	P 176	Herzog	P 176
Analysis Date:	28-Feb	28-Feb	28-Feb	28-Feb	5-Mar	5-Mar	5-Mar	5-Mar
Days Since Sampled:	9	9	9	9	14	14	14	14
	11.78	11.64	11.90	11.65	11.91	11.52	11.85	11.73
	11.56	11.68	11.65	11.96	11.56	11.66	11.68	11.74
	11.84	11.79	11.84	11.75	11.52	11.40	11.74	11.75
	11.54	11.89	11.56	11.62		11.43	11.68	11.55
	11.60	11.50	11.76	11.76	11.66	11.19	11.73	11.71
	11.60	11.60	11.64	11.92	11.56	11.06	11.72	11.56
Mean:	**11.65**	**11.68**	**11.73**	**11.78**	**11.64**	**11.38**	**11.73**	**11.67**
Standard Deviation:	0.125	0.139	0.130	0.138	0.158	0.219	0.063	0.093

Storage Temperature:	40°F	40°F	80°F	80°F	40°F	40°F	80°F	80°F
Method of Analysis:	Herzog	P 176	Herzog	P 176	Herzog	P 176	Herzog	P 176
Analysis Date:	19-Mar	19-Mar	19-Mar	19-Mar	19-Apr	19-Apr	19-Apr	19-Apr
Days Since Sampled:	28	28	28	28	59	59	59	59
	11.73	11.84	11.50	11.67	11.69	11.68	11.76	11.61
	11.67	11.61	11.69	11.79	11.52	11.66	11.75	11.28
	12.37	11.66	11.75	11.56	11.47	11.66	11.77	11.91
	11.48	11.57	11.80	11.44	11.70	11.25	11.90	11.85
	11.67	11.97	11.81	12.44	11.56	11.78	11.90	11.66
	11.58	11.48	11.82	11.50	11.71	11.69	11.93	12.00
Mean:	**11.75**	**11.69**	**11.73**	**11.73**	**11.61**	**11.62**	**11.84**	**11.72**
Standard Deviation:	0.316	0.183	0.122	0.368	0.105	0.187	0.083	0.261

Attachment E; Fuel Sample Weathering at Two Temperatures Measured by P 176 and the Herzog Methods



Attachment E

ENGINEERING OPERATIONS DIVISION

The Effect of Sampling Technique on the Measurement of Gasoline Volatility
The Effects of Purge Volume on the Measurement of Gasoline Volatility

Sampling Method	Tank Sample ASTM D 4057 section 9.2.3.1	Ambient Nozzle Sample no Purge	Ambient Nozzle Sample 3 gallon Purge
	12.32	12.26	12.29
	12.34	12.28	12.36
	12.34	12.29	12.27
	12.38	12.38	12.36
	12.36	12.42	12.42
	12.47	12.25	12.47
average	**12.37**	**12.31**	**12.36**
standard deviation	**0.054**	**0.070**	**0.076**

Ambient temperatures during samplings between 50 and 60 °F

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Attachment F

ENGINEERING OPERATIONS DIVISION

The Effect of Sampling Technique on the Measurement of Gasoline Volatility

Estimated Time for Various Sampling Scenarios

	Sampling Technique			
Activity	**ASTM**	**EPA**	**CARB**	**Ambient**
Overhead: (This aspect includes assembly of equipment and supplies at the base, unpacking and set-up at the site, obtaining one sample, repacking and return to the base)	2.0	1.0	0.7	0.5
Each add'l sample from the same tank or nozzle: (This includes storage and paperwork)	0.1	0.1	0.1	0.1
The first sample from a different source at the same location:	0.4	0.2	0.2	0.2

Notes: The times shown above are in hours and assume a team of two inspectors and include time for the storage and paperwork associated with each sample. Travel time and the actual analyses are not included.

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